Effects of operating parameters on the performance of washing–electrokinetic two stage process as soil remediation method for lead removal

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Title: Effects of operating parameters on the application of two-stage electrokinetic washing of soil for lead removal

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Abstract

The application of a two-stage electrokinetic washing system on remediation of lead (Pb) contaminated soil was investigated. The process consisted of an initial soil washing, followed by an electrokinetic process. The use of electrokinetic process in soil washing could provide additional driving force for transporting the desorbed Pb away from the soil even in the absence of pore flow. Thus, high usage of wash solution may be mitigated. In this study, the effect of operating conditions such as electric potential difference, wash solution concentration and initial Pb concentration on the feasibility of a two-stage electrokinetic washing on Pb removal was investigated using response surface methodology based on Box-Behnken design. The wash solution used was citric acid and three main aspects were examined, namely: i) removal efficiency, ii) effluent generated, and iii) power consumption. The results revealed that the increase in electric potential difference and wash solution concentration generally enhanced Pb removal efficiency and the interactions of these parameters were significantly positive. However, undesirable high effluent generation and power consumption were also caused by these increments. Optimisation study revealed that 84.14% removal efficiency with zero effluent generation and 2.27kWh/kg Pb removed could be achieved at 7.58V and 0.057M citric acid concentration. In comparison to normal soil washing, two-stage electrokinetic washing showed an enhancement in removal efficiency by ≈16% via electromigration under optimum conditions using similar solution: soil ratio of <0.8mL: 1g soil. The study reveals that incorporation of electrokinetic process in soil washing is feasible as it not only enhances Pb removal efficiency at minimum wash solution usage in comparison to normal soil washing, but also provides *in situ* Pb recovery in cathode chamber via electrodeposition.

Keywords: Soil remediation; lead; electrokinetic washing; response surface methodology

1. Introduction

Lead (Pb) is a highly toxic substance to living organisms. Its ability to bio-accumulate often causes acute and chronic illnesses which damage human body systems when it is inhaled and ingested [1-2]. Pb has been extensively used as a raw material in manufacturing processes such as ammunition, batteries, bearings, plumbing, ceramic glazes, weights, caulks, dyes, pigments and pesticides [2-3]. In order to support huge demand for Pb in the world, global Pb production as high as 10,654,000 tonnes was reported in 2012. As a result of its huge production and usage, human can be easily exposed to Pb via variety pathways. Soil contamination is one of the pathways for Pb exposure especially from industrial lands with the activities like battery manufacturing, gould casing, scrap Pb handling [4] as well as Pb smelting and mining [1-2]. High Pb concentration in the range of 751.98-138,000mg/kg was reported in the soil from these industries [3, 5-8]. Thus, a proper treatment to these soils is necessary.

Soil washing has been reported as one of the effective soil remediation methods for removing Pb and heavy metals [9]. However, it is worth noting that soil washing requires high amount of wash solution for effective treatment. A high solution: soil ratio of 3.33-20mL: 1g [10-12] shows the disadvantage of applying soil washing as the amount of spent wash solution that requires post treatment is large. In contrast, electrokinetic process could reduce the amount of wash solution needed in soil remediation. Electrokinetic process is one of the soil remediation methods that show great potential to remove organic compounds and heavy metals [13-15]. This process is conducted by inducing low magnitude direct current through the soil as the driving force for contaminants removal. [13, 15-16]. For metal ions removal, electromigration is the main mechanism for the transport in the soil under electric field influence towards their respective electrodes. It is worth noting that electromigration is independent of the pore fluid movement [13]. This suggests the potential of electrokinetic process to be incorporated into soil washing so that the wash solution usage in the remediation of high permeability soil could be reduced.

Electrokinetic process has been applied in the treatment of soils with high permeability [15, 17-21]. The work of Kim et al. [19] in treating Co and Cs contaminated sandy soil showed that electrokinetic process not only provided favourable removal efficiency but also lower effluent generation which was only 5% of the effluent generated by soil washing. Furthermore, Kim et al. [19-20] also reported further enhancement in the removal efficiencies of Co and Cs were achieved when electrokinetic process was incorporated into soil flushing. However, this was found to increase the effluent generation slightly in comparison to normal electrokinetic process. Recently, a study on the incorporation of electrokinetic process into soil washing as a two-stage electrokinetic washing for Pb removal from sandy soil has been investigated [22]. This process of soil remediation method which consisted of: i) initial soil washing, and ii) electrokinetic process was conducted at different stages in single equipment, as shown in Fig. 1 [22]. The process was initiated by filling up the anode chamber with wash solution such as $NaNO_3$, HNO_3, citric acid and EDTA while the cathode chamber was left empty. Due to hydraulic gradient difference between the chambers, soil washing occurred via the diffusion and advection of wash solution from anode chamber to the cathode chamber through the soil column. This provide a “flushing” effect for Pb desorption and transport to the cathode chamber during wash solution filling process. When the cathode chamber was completely filled up, soil washing stopped, as shown in Fig. 1. Then, a constant voltage was applied through the soil as second stage of the treatment by providing electrical driving forces to further transport Pb away from the soil while preventing local concentration polarisation for Pb desorption. Previous work showed that two-stage electrokinetic washing enhances soil remediation efficiency in comparison to soil washing [22]. Among the solutions investigated, citric acid was identified as the best wash solution as it had provided high enhancement in Pb removal efficiency mainly via electromigration even at low wash solution consumption of <1mL: 1g. This eliminated the disadvantage of soil washing having high wash solution consumption. However, it is worth noting that significant volume of effluent was still generated via electroosmosis, which is not desirable. Hence, in order to limit the electroosmosis while maintaining high removal efficiency, the effects of operating parameters such as electric potential difference and wash solution concentration must be evaluated.

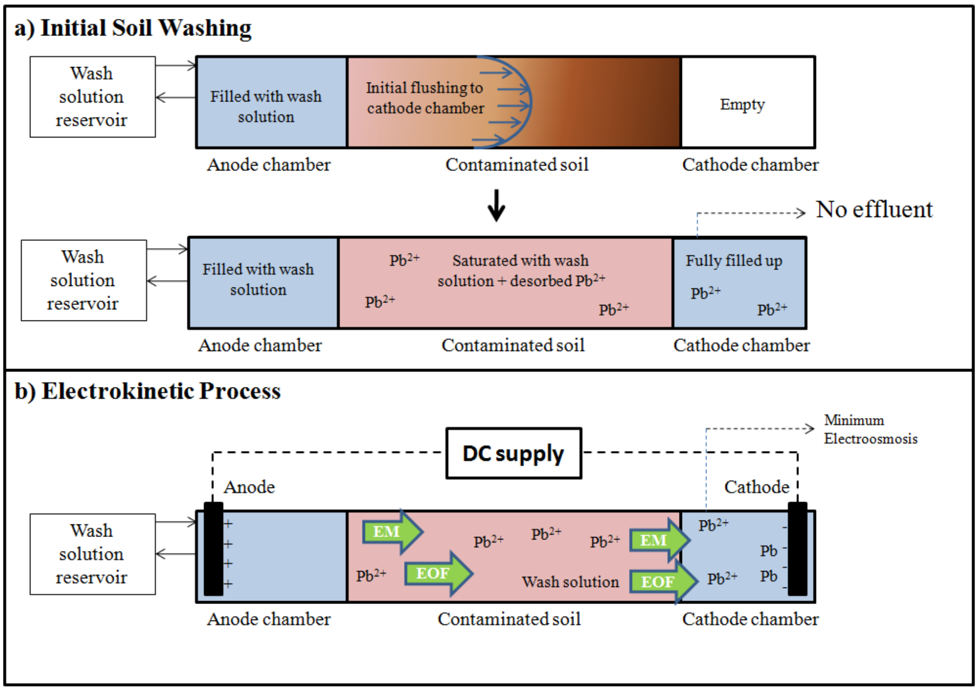

Fig. 1. Schematic diagram for two-stage electrokinetic washing [22]

The main goal of the present study is to investigate the effect of operating parameters such as electric potential difference, wash solution concentration and initial Pb concentration on the performance of two-stage electrokinetic washing process as soil remediation method for Pb removal. Unlike most of the studies for electrokinetic process, this study was conducted using statistical response surface methodology based on Box-Behnken Design such that the effects of the parameters and their mutual interactions can be adequately analysed. The performance of the system was evaluated for: i) removal efficiency, ii) effluent generated, and iii) power consumption. Finally, an optimisation test was conducted to investigate the possibility of two-stage electrokinetic washing to obtain high removal efficiency at negligible effluent generation and low power consumption.

2. Materials and Methods

2.1 Chemicals and soil

Table 1: The characteristics of the soil in this study

Soil properties	**Value**	**Method**
pH	3.97	USEPA SW-846 Method 9045D
Specific gravity	2.5	ASTM D 854 - Water pycnometer method
CEC (meq/100g)	5.1	Ammonium acetate method
Organic matter content	1.4%	Loss of weight on ignition
Soil metal content	**Concentration (mg/kg)**	**Method**
Iron	3719	USEPA 3050B
Aluminium	2400	
Manganese	185	
Magnesium	635	
Lead	11	
Zinc	18	

All the chemicals used in this study were of analytical grade and were supplied by R&M Chemicals, Malaysia. The soil used was taken from Hulu Langat, Malaysia and was sieved to a particle size of <0.85mm. The soil was classified as sandy soil according to USDA Soil Classification as it had 92% sand content, with 8% silt and clay. General properties of uncontaminated soil are as shown in Table 1. The soil had high iron (Fe) and mineral content and posed potential risk for Pb contamination via adsorption with a maximum contamination level of 1000mg/kg [23], which is higher than the regulatory limit in Malaysia [24]. In this study, artificially contaminated soil was prepared by spiking the soil with $Pb(NO_3)_2$ solution to create Pb contaminated soil with desired contamination level. The slurry was then homogenised using spatula and dried for one week. The contaminated soil was then stored in a dark place.

2.2 Response Surface Methodology

Response surface methodology (RSM) was used in this study to evaluate the effect of operating parameters on Pb removal in two-stage electrokinetic washing. RSM is a collection of mathematical and statistical techniques that are useful for modelling and analysis of problems for which a response on outcome is influenced by several variables and the objective of RSM is to optimise this response [26]. The use of RSM and Analysis of Variance (ANOVA) could give a suitable approximation for the true functional relationship between the response and the set of independent variables. In this study, a polynomial equation as shown in Equation (1) was generated, where y is the response, β is the regression coefficient, and x is the independent parameter [26].

$$y = \beta_0 + \sum_{i=1}^{3} \beta_i x_i + \sum_{i=1}^{3} \beta_{ii} x_i^2 + \sum_{i=1}^{2} \sum_{j=i+1}^{3} \beta_{ij} x_i x_j \qquad (1)$$

Box-Behnken Design was used in this study in combination with the Design Expert software. This design is a spherical three level design by combining 2^k factorial with incomplete block design and it is most efficient in terms of number of required runs in comparison to Central Composite Design [26]. Three parameters were investigated, namely electric potential difference (A), wash solution concentration (B) and initial Pb concentration (C). The levels of each parameter were coded as -1, 0 and 1 and the ranges of the parameters are shown in Table 2. The responses investigated in this study were i) removal efficiency, ii) effluent generated, and iii) power consumption. Based on Box-Behnken design, 17 experiments were conducted with five replicates of centre point experiments to estimate pure error for the models generated. The experiments were conducted in a random sequence to improve the precision of the experiments. The results obtained were then analysed using ANOVA and F-test with 95% confidence level. The numerical models generated from this method were used to analyse the importance of the parameters and their interaction effects. Finally, optimisation of these parameters was conducted based on the mathematical models generated.

Table 2: Experimental range and level of the parameters

Parameters	Symbol	Range and level		
		-1	0	1
Electric potential difference, V	A	7.5	18.75	30
Wash solution concentration, M	B	0.001	0.0505	0.1
Initial Pb concentration, mg/kg	C	400	700	1000

2.3 Experimental

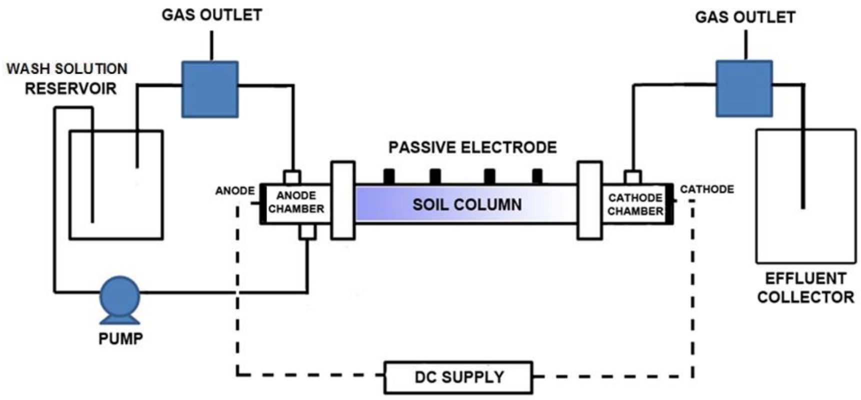

Fig. 2. Schematic diagram for the experimental setup [22]

Fig. 2 illustrates the schematic diagram for two-stage electrokinetic washing. A PTFE soil column with a dimension of 15cm length and 4cm diameter was used in the study. A mass of 250g of contaminated soil was compacted into the column slowly to yield an average soil voidage of 0.47. The anode and cathode chambers, each having a size of 4cm diameter and 7.4cm length were connected to two ends of the column and they were separated from the soil column by filter papers. Then, cylindrical graphite electrodes discs were installed at the other ends of the chambers. In this study, the overflow level for cathode chamber was adjusted to ≈0.6cm higher than the overflow level for anode chamber to ensure that the effluent flushed out was mainly attributed to electroosmosis only. Citric acid was chosen as the wash solution in this study due to its ability to provide high removal efficiency with stable system performance in the previous study [22]. The solution was pumped into the anode chamber from the bottom of the chamber at a rate of 15mL/min while the cathode chamber was left empty. Soil washing process was initiated when citric acid was transported through the soil column and filled up the cathode chamber as a result of a hydraulic head gradient between the chambers. This process faded once the cathode chamber was fully filled up. Then, second stage of treatment was initiated by applying constant voltage across the soil via the electrodes in the chambers as secondary driving force to further transport the desorbed Pb from the soil to the cathode chamber. The experiment was conducted for 24 hours. The details of the experiments based on Box-Behnken design as well as the results obtained are as shown in Table 3.

2.4 Analytical Methods

Electric current across the soil was determined during the experiments by Multimeter Sunwa TE-832B. The soil was sliced into five sections which were dried before property estimation. Soil pH at each section was determined by USEPA SW-846 method 9045D and was analysed using a calibrated pH meter (Crison Multimeter MM26+). Pb concentration in the soil section was extracted using KSTM method, as reported by Kim et al. [27]. The supernatant obtained from the method mentioned above was analyzed using ICP-OES for determining Pb concentration. Based on the analysis, the removal efficiency provided by two-stage electrokinetic washing was calculated using Equation (2), where C_0 was the initial Pb concentration in soil and C_t was Pb concentration that remained in soil after the experiment. The power consumption for the system was determined using Equation (3), where E is the power consumption per kg Pb removal, V is the electric potential difference used, I is the current of the system, t is the experiment duration and m_{Pb} is the mass of Pb removed.

$$\text{Removal Efficiency, \%} = \frac{C_0 - C_t}{C_0} \times 100 \tag{2}$$

$$E = \frac{1}{m_{Pb}} \int_0^t VI.dt \tag{3}$$

3. RESULTS AND DISCUSSION

3.1. ANOVA Analysis

Table 3: Details of the experiments using Box-Behnken design and the results obtained

Run	A, Electric potential difference, V	B, Wash solution concentration, M	C, Initial Pb concentraiton, mg/kg	Removal efficiency, %	Effluent generated, mL	Power consumption, kWh/kg Pb removed	*Average current, mA
1	18.75	0.0505	700	86.29	2.25	25.45	8.65
2	7.5	0.001	700	53.99	0	1.06	0.55
3	18.75	0.1	400	78.60	27.7	51.17	9.30
4	30	0.0505	1000	96.98	115.3	45.04	16.01
5	7.5	0.1	700	77.38	0	4.22	3.31
6	7.5	0.0505	1000	82.93	0	1.69	2.15
7	18.75	0.001	1000	84.52	0	6.23	2.93
8	18.75	0.0505	700	82.78	4.35	25.55	8.37
9	18.75	0.1	1000	90.79	27	21.49	11.40
10	18.75	0.0505	700	84.85	1.50	24.82	8.31
11	18.75	0.001	400	58.24	0	14.11	1.82
12	30	0.001	700	83.72	0	21.98	4.33
13	18.75	0.0505	700	85.19	3	25.37	8.58
14	30	0.1	700	94.62	103.35	79.53	18.61
15	18.75	0.0505	700	84.07	6.25	26.68	8.75
16	7.5	0.0505	400	61.12	0	5.82	2.11
17	30	0.0505	400	88.34	43.5	92.48	12.02

* The electric current was stable throughout the experiment. Thus, average current was used for analysis.

The experimental design and the results for: i) removal efficiency, ii) effluent generated, and iii) power consumption are as shown in Table 3. These results were analysed using ANOVA statistical models and Table 4 shows an example of the ANOVA analysis for removal efficiency, which is the main response in this study. The F-statistic is used to test the significance of each parameter and their interactions.

Table 4 shows that the model has F-Value of 79.22 with a (Prob > F) of <0.0001. This implies that the model is significant. Among the model parameters, A, B, C, B^2, AB, AC, BC are significant terms as they have (Prob >F) value of <0.05, which shows 95% of confidence level. The “Lack of fit” value of 3.27 with a (Prob >F) value of 0.1388 further suggests that there is 13.88% probability that the “Lack of Fit” value this large could occur due to noise, which is desired for the model. Moreover, a reasonable difference between the predicted and adjusted R^2 <0.2 [28] and adequate precision/ signal to noise ratio of > 4 [29] also indicate the adequacy of the model. The validity of the model was further tested from the aspect of normal probability plot and no apparent problem was found. A reasonably close value between the predicted and experimental results, as shown in Fig. 3a validates the accuracy of the models. Similar ANOVA analysis is also conducted for effluent generated as well as power consumption and appropriate models which predict the results well are obtained (Figs. 3b and 3c). The coded statistical models generated from ANOVA for removal efficiency, effluent generated, and power consumption are described by Equations (4), (5) and (6), respectively.

$$\begin{aligned}\text{Removal Efficiency, \%} = {} & 84.28 + 11.03A + 7.62B + 8.62C - 1.5A^2 - 5.8B^2 \\ & - 3.12AB - 3.29AC - 3.52BC\end{aligned} \tag{4}$$

$$\begin{aligned}\text{Effluent generated, mL} = {} & 3.47 + 39.70A + 13.68B - 0.18C + 24.2A^2 - 1.83B^2 \\ & + 12.03C^2 + 25.84AB + 17.95AC + 12.16A^2B + 18.13A^2C \\ & - 13.86AB^2\end{aligned} \tag{5}$$

$$\begin{aligned}\ln(\text{power consumption/kg Pb removed}) = {} & 3.24 + 1.5A + 0.65B - 0.42C - 0.61A^2 \\ & - 0.39B^2 + 0.021C^2 - 0.024AB + 0.13AC - 0.068A^2C\end{aligned} \tag{6}$$

Table 4: ANOVA analysis for removal efficiency

	Sum of Square	DF	Mean Square	F-Value Value	Prob > F	
Model	2319.02	8	289.88	79.22	< 0.0001	significant
A	973.29	1	973.29	265.99	< 0.0001	
B	463.91	1	463.91	126.78	< 0.0001	
C	593.75	1	593.75	162.27	< 0.0001	
A^2	9.45	1	9.45	2.58	0.1467	
B^2	142.09	1	142.09	38.83	0.0003	
AB	39.00	1	39.00	10.66	0.0114	
AC	43.36	1	43.36	11.85	0.0088	
BC	49.63	1	49.63	13.56	0.0062	
Residual	29.27	8	3.66			
Lack of Fit	22.42	4	5.60	3.27	0.1388	Not significant
Pure Error	6.85	4	1.71			
Cor Total	2348.30	16				
Std. Dev.	1.91		R-Squared	0.99		
Mean	80.85		Adj R-Squared	0.98		
C.V.	2.37		Pred R-Squared	0.90		
PRESS	229.07		Adeq Precision	31.56		

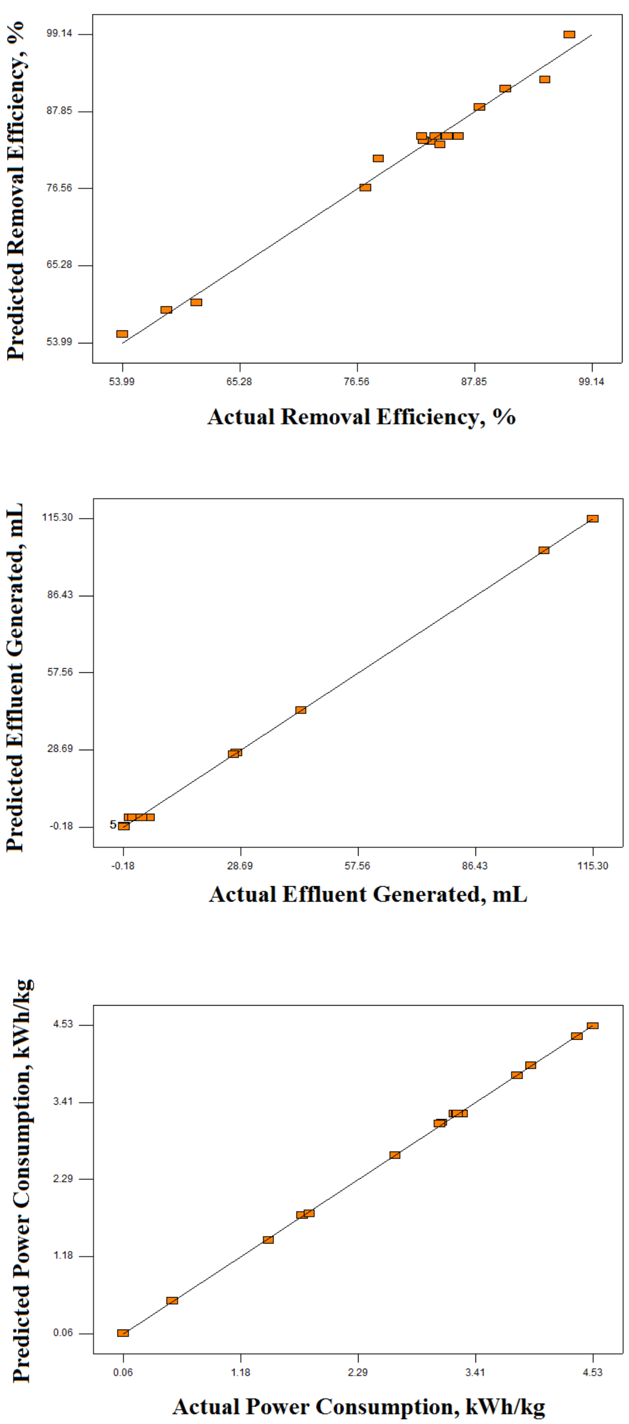

Fig. 3. Comparison between predicted value from the statistical models and actual experimental results for: a) removal efficiency, b) effluent generated, c) power consumption

3.2 Removal Efficiency

The response surface plot for removal efficiency under different operating parameter levels based on the statistical model in Equation (4) is shown in Fig. 4. The plots reveal that electric potential difference, wash solution concentration and initial Pb concentration have positive effects on the removal efficiency. Figs. 4a and 4b shows that electric potential difference is proportional to the removal efficiency, regardless of the other two parameters. In the navigation space, an increase in electric potential difference from 7.5V to 30V is observed to enhance the removal efficiency steadily from 53.99% to 83.72% and 77.38% to 94.62% when wash solution concentration used are 0.001M and 0.1M, respectively. The use of higher electric potential difference promotes higher removal efficiency by mainly enhancing electromigration rate via higher current and electric field strength through the soil. This is due to the fact that electromigration rate for metal ions is directly dependent on the electric field strength, as shown in Equation (7) where v_{EM} is the velocity for electromigration/ion transport, u is the ionic mobility and E is the magnitude of electric field strength, E [16, 30]. This observation was also in line with other works on the removal of heavy metals by electrokinetic process whereby higher electric potential difference was reported to improve the migration and removal efficiency [31-33].

$$v_{EM} = u.E \qquad (7)$$

In addition, wash solution concentration also showed positive impact on the removal efficiency. As shown in Fig. 4a, when electric potential difference is constant, the increase in wash solution concentration from 0.001M to 0.1M steadily enhances the removal efficiency. When other parameters were held constant, the increase in citric acid concentration not only provided higher Pb desorption via higher amount of H^+ ions for desorption enhancement [34-35], but also prevented the increase of pH in the cathode chamber, which further prevent the reduction in Pb electromigration due to hydroxide precipitation process at cathode region [36]. Moreover, citric acid was also reported to increase Pb solubility via water soluble complex formation [37]. It was also worth noting that citric acid could promote dissolution of Fe and Al, which were the binding sites for Pb, from soil surface [22]. All of these mechanisms could contribute to the improvement in Pb desorption and removal efficiency. However, Fig. 4a also suggests that the effect of wash solution concentration is more significant at low electric potential difference. As the electric potential difference was increased from 7.5V to 30V, the enhancement caused by the increment in wash solution concentration from 0.001M to 0.1M was 23.39% and 10.9%, respectively. Moreover, the effect of wash solution is optimum at a concentration of 0.075M for any electric potential difference used, as shown in Fig. 4a. Further improvement on the removal efficiency can only be achieved by increasing electric potential difference for better Pb desorption and electromigration rate. Thus, it is suggested that high removal efficiency could be attained by fine tuning the electric potential difference and wash solution concentration. This is especially important when both efficiency and cost are to be considered.

The study also suggests that two-stage electrokinetic washing is suitable for the soil with high contamination level as higher removal efficiency is observed in the case of higher initial Pb concentration when other parameters are held constant, as illustrated in Figs. 4b and 4c. This is mainly due to the removal of higher amount of Pb under high initial Pb concentration. In terms of Pb residual in the soil, initial Pb concentration did not show significant effect. The residual Pb concentration in the soil after the experiments remained close when treating soil with different initial Pb concentrations, as shown in four cases, which were i) Tests 11 vs 7 (171mg/kg vs 163mg/kg), Tests 3 vs 9 (88mg/kg vs 97mg/kg), iii) Tests 17 vs 4 (48mg/kg vs 32mg/kg) and iv) Test 16 vs 6 (160mg/kg vs 180mg/kg). This observation suggests that the amount of residual Pb after the treatment was generally less dependent of initial Pb concentration, even though higher removal efficiency was achieved.

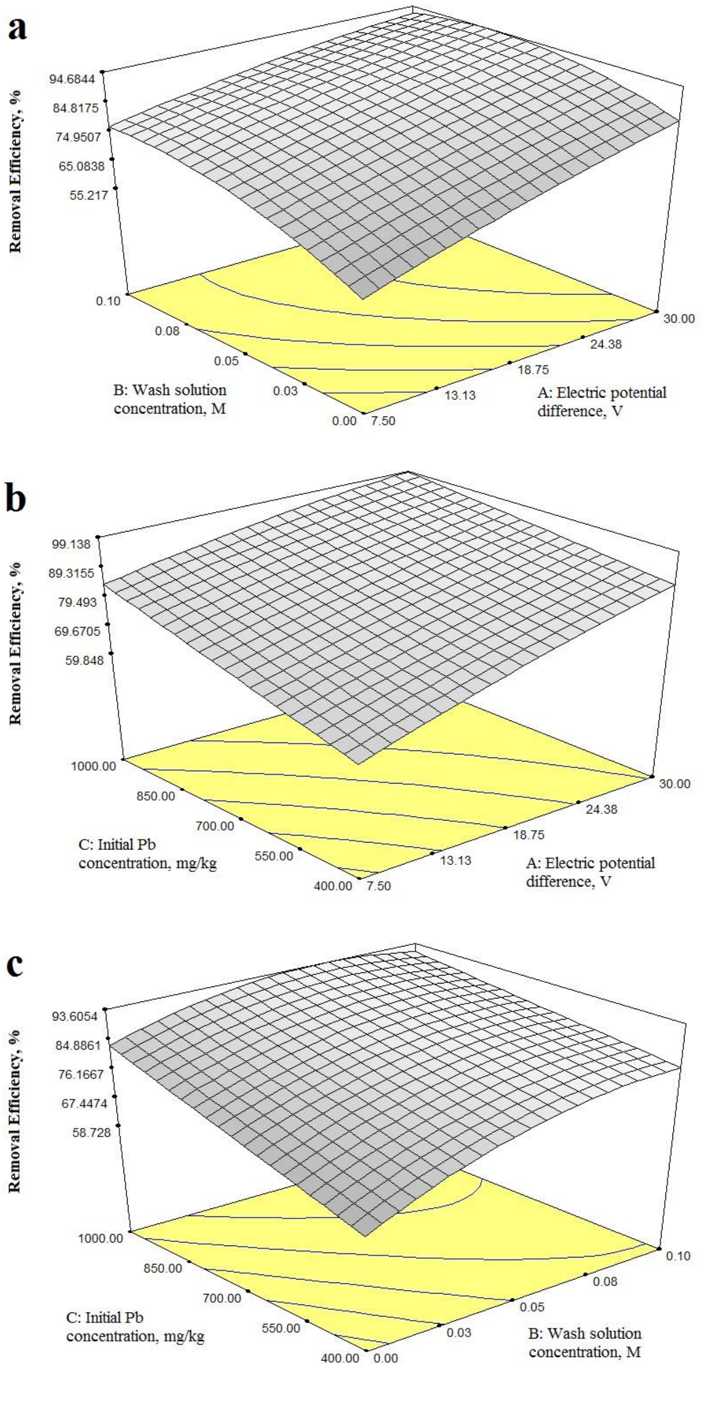

Fig. 4. Interaction effect of parameters on Pb removal efficiency: a) electric potential difference and wash solution concentration (initial Pb concentration: 700mg/kg); b) electric potential difference and initial Pb concentration (wash solution concentration: 0.0505M); c) wash solution concentration and initial Pb concentration (electric potential difference: 18.75V)

3.3 Effluent generated

The interaction plots shown in Fig. 4 illustrate that high removal efficiency could be achieved using high electric potential difference with high wash solution concentration. However, it may be noted that the generation of high electric field/current under this condition can induce high electroosmosis, resulting in higher effluent generation. Even though electroosmosis may also contribute to Pb removal efficiency, this is not favoured as it entails higher cost for spent wash solution treatment. Thus, the effect of the above mentioned parameters on effluent generation was investigated so that an optimisation of two-stage electrokinetic washing could be performed based on both technical and economic considerations.

The experimental setup was configured based on minimising the effluent flow from hydraulic gradient. Thus, the amount of effluent collected in this work was mainly attributed to electroosmosis only. Helmholtz-Smoluchowski theory as shown in Equation (8) suggests that the electroosmotic flow (EOF) velocity, v_{EO} (m/s), is directly proportional to permittivity of a vacuum, ε_0, electric field of the system, E, dielectric constant of the solution, D, zeta potential of the soil, ξ, and inversely proportional to dynamic viscosity of the solution, η [16, 38-39]. In this work, the electric field strength showed higher impact than soil zeta potential, considering that the average soil pHs for the tests were stable within the range of 2.66-3.35, as a result of negligible base front effect. Thus, the effect of soil zeta potential difference was relatively small.

$$v_{EO} = -\frac{D\varepsilon_0\xi}{\eta}E \qquad (8)$$

The results in Table 3 show that EOF is not significant or low (<7mL) in most of the cases, except for Tests 3, 4, 9, 14 and 17, which are under two conditions: i) electric potential difference of ≥18.75V, and ii) wash solution concentration of ≥ 0.0505M. These conditions shared one similarity, which is they have electric current of >9mA, as shown in Table 3. The volume of effluent generated by EOF is found to be dependent on the electric current, whereby the higher current produces more effluent, as shown in Table 3.

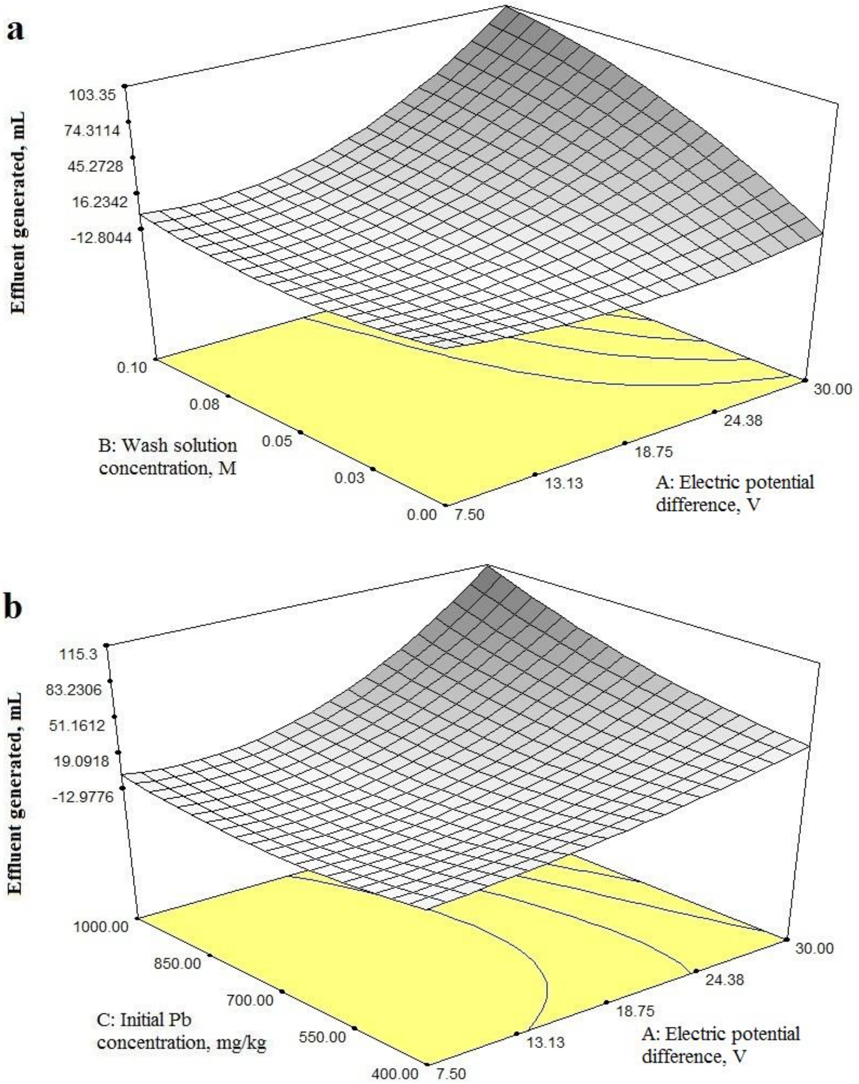

Fig. 5. Interaction effect of parameters on the amount of cumulative effluent generated: a) electric potential difference and wash solution concentration (initial Pb concentration = 700mg/kg); b) electric potential difference and initial Pb concentration (wash solution concentration = 0.0505M)

The response surface plots as shown in Fig. 5 suggest that electric potential difference is the most dominant factor that influences effluent generation in comparison to the other two. This was also reported by Zhou et al. [33] whereby the increase in electric potential difference increased the electroosmosis. However, it was also noted that the effect of electric potential difference was also dependent on wash solution concentration as well as initial Pb concentration. Fig. 5a reveals that at wash solution concentration of 0.001M, the increase in electric potential difference does not cause effluent generation. This could be due to relatively low electric current generated at low citric acid concentration (maximum ≈4mA), which indicated high electrical resistance in the overall system. When the wash solution concentration was increased, the reduction of EOF, as a result of the compression of the diffuse double layer thickness at higher ionic strength solution [13, 40-41] was not observed. Instead, an increase in electric current is observed when the wash solution concentration and initial Pb concentration are increased from 0.001M to 0.1M and 400mg/kg to 1000mg/kg, respectively (Table 3), and higher amount of effluent is obtained, especially at high electric potential difference (≥18.75V), as shown in Table 3 and Fig. 5. This was also in line with the works of Yang and Long [42] and Kim et al. [43] which reported that higher electroosmosis was achieved when the current density across the system was enhanced. Nevertheless, the effect given by wash solution concentration and initial Pb concentration is less significant when electric potential difference is low, as shown in Fig. 5.

3.4 Power Consumption

The ANOVA shows that the power consumption is an exponential function for the parameters studied, as shown in Equation (6). The response surface curve of ln(power consumption/kg Pb removed) versus the above-mentioned parameters, as illustrated in Fig. 6a, show that the use of higher electric potential difference and wash solution concentration increase the power consumption. This was mainly due to high electric current available as a result of higher electrical driving force and higher amount of ions available via electrolysis and wash solution concentration. This not only enhanced Pb transport towards the cathode chamber, but also the transport of non-targeted ions such as H^+, Fe, Al and other ions that are dissolved, which consumed unnecessary electrical power. Hence, it could be said that excessive increases in electric potential difference and wash solution concentration to enhance removal efficiency are not attractive options, as it in turn adversely the process feasibility. On the other hand, higher initial Pb concentration is found to reduce the power consumption, as shown in Fig. 6b. This suggests that two-stage electrokinetic washing is more economical for treating highly contaminated soil.

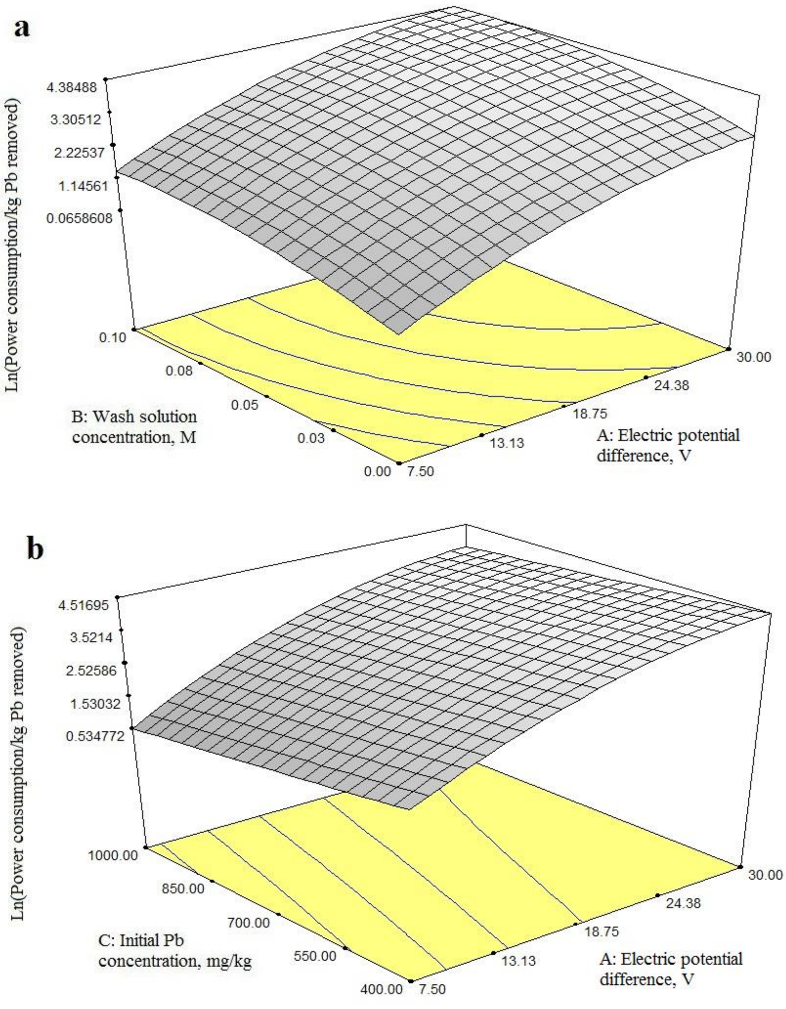

Fig. 6. Interaction effect of parameters on power consumption: a) electric potential difference and wash solution concentration (initial Pb concentration: 700mg/kg); b) electric potential difference and initial Pb concentration (Wash solution concentration: 0.0505M)

3.5 Optimization Study

The results discussed in Sections 3.2 to 3.4 suggest that higher Pb removal efficiency can be achieved at high electric potential difference and wash solution concentration. However, the increase in the value of these parameters also caused undesirable effluent generation via electroosmosis and high power consumption. An optimisation study was carried out based on the statistical models presented. This was aided by the desirability function in Design Expert 6.0.1 software so that the optimum Pb removal efficiency given by two-stage electrokinetic washing at efficient low power consumption and low effluent generation could be determined. Optimum operating parameters for electric potential difference and wash solution concentration were investigated for 1000mg/kg Pb contaminated soil, which was at the highest Pb contamination level. Three constraints in the process were set at: i) lowest power consumption, ii) lowest effluent generation, and iii) maximum removal efficiency. The analysis suggested that a combination of electric potential difference of 7.58V and wash solution concentration of 0.057M had the highest desirability of 0.887. This was expected to give 84.58% removal efficiency with a power consumption of 1.89kWh/kg Pb removed and negligible effluent generation.

An experiment was conducted based on the conditions given for validation purpose. Table 5 shows that the experimental result of 84.14% removal efficiency is in close agreement with the predicted result with an error of less than 1%. The power consumed under this condition was 2.27kWh/kg Pb removed and no effluent was detected during the experiment.

Table 5: Predicted and experimental results for removal efficiency, effluent generated and power consumption under the optimum conditions

Parameters	Predicted Value	Experimental
Electric potential difference, V	7.58	7.58
Wash solution concentration, M	0.057	0.057
Effluent generated, mL	0.017	0
Removal efficiency, %	84.58	84.14
Power consumption, kWh/kg Pb	1.89	2.27

3.6 Performance of two-stage electrokinetic washing under optimum conditions

A comparative study of the performance of two-stage electrokinetic washing and normal soil washing (without application of electricity) was made using the optimum conditions obtained in Section 3.5. Table 6 shows that, in general, two-stage electrokinetic washing enhanced the removal efficiency to ≈84% in comparison to normal soil washing (≈68%) when 0.057M citric acid concentration was used at similar low solution: soil ratio of <0.8mL: 1g where the volume of wash solution used was attributed to soil saturation and cathode chamber filling. The application of constant voltage of 7.58V supported electromigration of Pb in the soil after initial soil washing stage even though the pore flow was absent. Besides enhancing Pb removal efficiency, the results also suggested that the application of low magnitude electricity across the soil for 24 hours provided stable system condition. A stable low electric current as shown in Fig. 7a provides minimum change in the recorded pHs in wash solution chambers (anode and cathode chambers) and the soil pH, as shown in Table 6 and Fig. 7b. This observation confirmed that the effect of electrolysis and base front in cathode chamber were minimum in this process as citric acid served as a buffer solution in the cathode chamber to prevent pH change in soil and cathode chamber.

Table 6: Comparison of removal efficiency and wash solution chambers' pHs between normal soil washing and two-stage electrokinetic washing

	Soil washing	**Two-stage electrokinetic washing**
Removal efficiency, %	≈68%	≈84%
pH in anode chamber	2.17	2.14
pH in cathode chamber	2.13	2.23

The use of 0.057M citric acid in two-stage electrokinetic washing was found to provide one way electromigration for Pb. As shown in Fig. 7c, two-stage electrokinetic washing results in lower Pb residual than normal soil washing in any soil sections, suggesting that one way Pb electromigration towards the cathode chamber is the main mechanism during electrokinetic process whilst electroosmosis in these conditions is insignificant. This is in agreement with the proposed mechanism suggested in a previous investigation when citric acid was used as the wash solution in a two-stage electrokinetic washing [22].

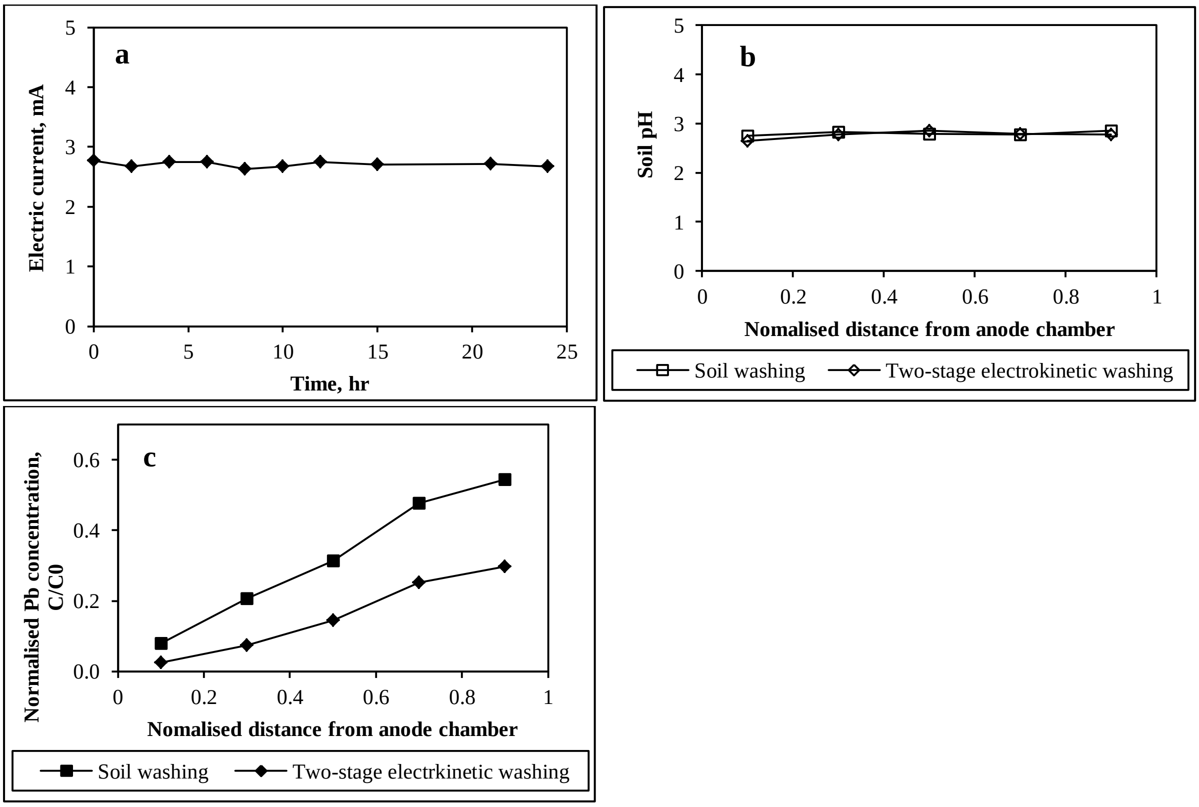

Fig. 7. (a) Change of electric current across the soil at different time; (b) soil pH at different soil sections after the experiments; (c) normalised Pb concentration at different soil sections after the experiments

The application of electricity was also found to cause electrodeposition on cathode. As shown in Fig. 8, grey solid was found to be deposited on the cathode after the experiment while the anode was free from corrosion and deposition. The deposit was dissolved in 0.1M HNO_3 for Pb content analysis. It was found that 49% of Pb in the contaminated soil was electrodeposited on the cathode surface after 24 hours experiment under the optimum conditions. Thus, it can be suggested that two-stage electrokinetic washing not only favours enhancement in Pb removal efficiency in comparison to normal soil washing but also facilitates *in situ* Pb recovery from the solution in the cathode chamber via electrodeposition.

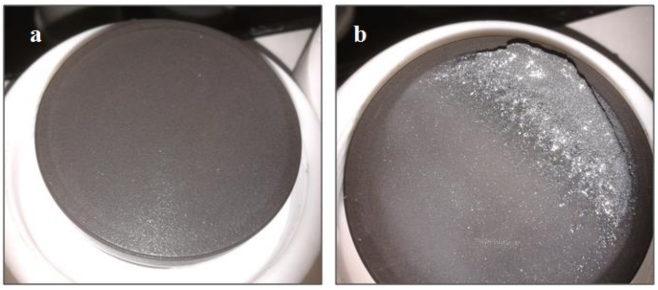

Fig. 8. Physical observation on (a) anode and (b) cathode after the experiment based on optimum conditions

4. Conclusions

Incorporation of electrokinetic process in soil washing as a two-stage electrokinetic washing was investigated in this study to remove Pb from sandy soil. The effects of operating parameters such as electric potential difference, wash solution (citric acid) concentration and initial Pb concentration were investigated on i) Pb removal efficiency, ii) effluent generated, and iii) power consumption. Unlike other studies, the effect of operating parameters was evaluated using response surface methodology based on Box-Behnken Design. From the study, several conclusions could be made:

i) Pb removal efficiency was strongly dependent on electric potential difference and wash solution concentration. The increase in these parameters increased Pb removal efficiency, and the interaction among these parameters was significantly positive.

ii) However, the increase in electric potential difference and wash solution concentration increased effluent generation (via electroosmosis) and power consumption, as a result of the increase in electric current.

iii) Optimisation study based on the response surface plots showed that at optimum operating conditions of 7.58V and 0.057M wash solution concentration, Pb removal efficiency of ≈84% was achieved at negligible electroosmosis and a power consumption of 2.27kWh/kg Pb removed. In comparison to normal soil washing, an enhancement in removal efficiency by ≈16% was achieved by two-stage electrokinetic washing at low solution: soil ratio (<0.8mL:1g). Furthermore, electrokinetic process also facilitated *in situ* Pb recovery in cathode chamber via electrodeposition.

iv) Incorporation of electrokinetic process in soil washing is a feasible soil remediation process as it not only enhances Pb removal efficiency at minimum wash solution usage in comparison to normal soil washing, but also provides *in situ* recovery of Pb in cathode chamber via electrodeposition. Nevertheless, the feasibility of this system in treating other types of soil, as well as real contaminated soils should be further evaluated in the future works.

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